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(54) Title: PROCESS FOR OLIGOMERIZING C ₃ AND HIGHER OLEFINS USING ZIRCONIUM ADDUCTS AS CA- TALYSTS (57) Abstract C ₃ and higher olefins are oligomerized using a two component catalyst system comprising (a) a soluble adduct of zir- conium tetrahalide, the halogen being Br or Cl, with an organic compound selected from the group of esters, ketones, ethers, amines, nitriles, anhydrides, acid chlorides, amides or aldehydes, the organic compound having up to about 30 carbon at- oms and (b) an alkyl metal selected from the group R ₂ AlX, RAlX ₂ , R ₃ Al ₂ X ₃ , R ₃ Al and R ₂ Zn where R is C ₁ -C ₂₀ alkyl and X is Cl or Br. ZrCl ₄ adducts with organic acetates are the preferred embodiments. Dimers, trimers and tetramers are selec- tively prepared in the process.		

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PROCESS FOR OLIGOMERIZING C₃ AND
HIGHER OLEFINS USING ZIRCONIUM
ADDUCTS AS CATALYSTS

This invention relates to an improved process for oligomerizing C₃ and higher olefins. More particularly, this invention relates to the production of such oligomers of higher olefins utilizing an adduct of zirconium tetrahalides as an essential part of the homogeneous catalyst system.

The oligomerization of ethylene to produce linear alpha-olefins is generally known in the art. The use of zirconium-containing catalysts is disclosed, for example, in U.S. Patents 4,486,615; 4,442,309; 4,434,313; 4,434,312; 4,410,750; 4,409,409; 4,396,788; 4,377,720 and 4,361,714. A number of these patents disclose reaction products of zirconium halides to provide zirconium alkoxides or carboxylates, such as U.S. Patents 4,409,409 and 4,486,615 which show various derivatives of tetravalent zirconium. The concept of the present invention, use of zirconium tetrahalide (bromide, chloride or mixtures thereof) adducts of certain organic compounds, preferably certain alkyl acetate esters, as a catalyst for oligomerization of C₃ and higher olefins, is not disclosed by these references.

Japanese Application 60-137683, filed June 25, 1985 by Shiroki et al. and published January 6, 1987 as Japanese Kokai 62-000430, discloses the production of linear alpha-olefins by polymerizing ethylene in the presence of a mixture consisting of a zirconium halide, an alkyl aluminum halide and a compound which may be that of sulfur or that of nitrogen. The catalyst is described as a three component catalyst.

U.S. Patent 3,622,552, issued November 23, 1971 to Fukuda et al. discloses the preparation of crystalline homo- or co-polymers of olefin using a three component catalyst comprising (1) an organoaluminum compound of the formula AlR_2X , R being a hydrocarbyl, X being halogen, (2) a Group IV, V or VI transition metal halide and (3) a saturated or unsaturated carboxylic ester having a side chain on a carbon atom in alpha position to ester carbon atoms. Fukuda et al. do not disclose the preparation of linear alpha-olefin oligomers and do not disclose the formation of a homogeneous two component catalyst, one component of which being an adduct of zirconium tetrahalide with an organic compound.

U.S. Patent 4,855,525, issued August 8, 1989, to the inventors hereof, discloses the use of zirconium tetrahalide adducts as catalysts for the production of linear alpha-olefins from ethylene. The present invention is based on the discovery that the same zirconium halide adduct catalyst system may be effectively used to oligomerize other olefins, namely C_3 and higher olefins.

The present invention is concerned with a process comprising the use of homogeneous catalyst system for conducting the oligomerization of propylene and higher olefins. In the present invention the objective is toward the production of dimers, trimers or tetramers of the olefins and not the production of high molecular weight, crystalline polymers.

The present invention provides a number of desirable advantages: the catalyst is readily prepared and is soluble, it may be used in high concentrations, it is storage stable and use of the novel adduct catalyst system provides principally branched products with suitable conversions of C_3 and higher olefins. The solubility of the novel catalyst of this invention enables the catalyst to be fed to the reaction vessel in an easily

controlled liquid stream. Importantly the exhibits complete solution into the reaction solution and all the zirconium is available for catalysis in contrast to prior art techniques wherein zirconium was added as a partially soluble salt.

In accordance with the present invention there has been discovered a process for oligomerizing C_3 and higher olefins in the presence of a homogeneous two component catalyst, the first component being an adduct of $ZrCl_aBr_b$, where $a+b=4$ and a or b may be 0, 1, 2, 3 or 4, with an organic compound selected from the group consisting of esters, ketones, ethers, amines, nitriles, anhydrides, acid chlorides, amides or aldehydes, said organic compound having up to 30 carbon atoms, and the second component being an alkyl metal catalyst selected from the group consisting of R_2AlX , RA_2X_2 , $R_3Al_2X_3$, R_3Al and R_2Zn wherein R is C_1 - C_{20} alkyl and X is Cl or Br , the oligomerization being conducted in a reactor vessel at $50^\circ C$ to $300^\circ C$ at a suitable pressure (depending on the olefin used) of about 15 to 5,000 psig in the liquid phase.

Suitable olefins which may be oligomerized in accordance with the present invention include those having about 3 to 20 carbon atoms, such as propylene, butylene, hexene, decene, tetradecene and the like, including both linear and branched olefins. Particularly preferred are aliphatic, monounsaturated linear hydrocarbyl unsubstituted 1-olefins such as propylene-1, butene-1, hexene-1, decene-1, and tetradecene-1 which have about 3 to 20 carbon atoms. The invention is also considered applicable to aromatic or cycloaliphatic olefins capable of being oligomerized such as styrene, 4-vinylcyclohexene and dicyclopentadiene.

The products of this invention have a number of uses. They are particularly useful as feedstocks for

hydroformylation and hydrogenation in order to prepare high molecular weight alcohols having a specific molecular weight. Such alcohols are used for preparation of plasticizers and surfactants and detergents. For example, 1-decene may be dimerized to C₂₀ olefin which may be hydroformylated and hydrogenated to prepare a C₂₁ alcohol, which may be ethoylated to provide a useful surfactant. Also, 1-decene may be trimerized and tetramerized to make C₃₀/C₄₀ olefins which may then be hydrogenated to make synthetic basestocks for lubricants.

An essential aspect of the present invention is that the first component of the catalyst is an adduct of zirconium tetrahalide, the halogen being Br or Cl or a mixture of said halides, with certain organic compounds. The second component of the catalyst, which is an alkyl aluminum or alkyl zinc compound, is well known in the art and has been used conventionally in ethylene oligomerization processes as a co-catalyst component.

The first component of the catalyst may be an adduct of ZrCl₄Br₄ with an ester, a ketone, an ether, an amine, a nitrile, an anhydride, an acid chloride an amide or an aldehyde and these various adduct-forming organic components may have up to about 30 carbon atoms. The adducts generally include mole ratios of organic component to zirconium of from about 0.9 to 1 up to about 2 to 1. Preferred are equimolar adducts. The adduct must be soluble in and stable in the solvent which is used as the reaction medium for the oligomerization process of the present invention.

Adducts may be formed from ZrCl₄, ZrBr₄, as well as the mixed tetrahalides: ZrClBr₃, ZrCl₂Br₂ and ZrCl₃Br, wherein the halogen is limited to Cl or Br. ZrCl₄ adducts are especially preferred.

Preferred are adducts of ZrCl₄ with esters of the general formula R₁COOR₂ where R₁ and R₂ may be alkyl,

aryl, alkaryl or aralkyl groups having a total of 1 to 30 carbon atoms and R_1 may also be hydrogen. R_1 and R_2 taken together may also represent a cycloaliphatic group and the ester may be compounds such as gammabutyrolactone or phthalide. Especially preferred are alkyl acetate esters where the alkyl group has 6 to 16 carbon atoms such as n-hexyl acetate, n-heptyl acetate, n-octyl acetate, n-nonyl acetate, n-decyl acetate, isohexyl acetate, isodecyl acetate, and the like which have been found to form discrete dimeric equimolar adducts with $ZrCl_4$. This particularly preferred embodiment may be represented by the formula $(ZrCl_4 \cdot CH_3COOR_1)_2$ where R_1 is a C_6 to C_{16} alkyl or a mixture of C_6 to C_{16} alkyls. These preferred ester adducts are capable of providing highly concentrated solutions in the solvent used as the reaction solvent, i.e., up to about 40% by weight of $ZrCl_4$, when preferred mixed isomers of isodecyl acetate esters are used. Particularly useful are mixtures of various isomers of isohexyl, isoheptyl, isooctyl, isononyl, isodecyl or isotridecyl acetate sold by Exxon Chemical Company, respectively, as Exxate® 600, Exxate® 700, Exxate® 800, Exxate® 900, Exxate® 1000 and Exxate® 1300. The isohexyl acetate mixture comprises about, by weight, 36-38% n-hexyl acetate, 18-20% 2-methyl-1-pentyl acetate, 22-24% 3-methyl-1-pentyl acetate and 16-18% 4-methyl-1-pentyl acetate as principal compounds. Exxate® 1000 isodecyl acetate mixture is a complex mixture of isomers and gas chromatographic analysis shows about 100 different isomers being present, none of which are greater than about 12% by weight of the mixture. Exxate® 1000 has a boiling point range of about 425°F to 482°F (95% distilled).

These adducts have been prepared by simple addition of the organic ester to a slurry of $ZrCl_4$ in the inert organic or alpha-olefin solvent. The ester is added

slowly to the stirred mixture at room temperature and complete formation and dissolution of the adduct is observed after several minutes. The dissolution is exothermic and the mixture reaches a temperature of about 50°C as a result of the heat of reaction due to adduct formation.

Also suitable, for providing soluble zirconium adducts useful as the first component catalyst of the present invention are ketones, ethers and aldehydes which may be represented, respectively, by the formulas: $R_1C(:O)R_2$, R_1OR_2 and $R_1C(:O)H$ where R_1 and R_2 represent alkyl, aryl, alkaryl or aralkyl groups, the total of R_1 and R_2 being not more than about 30 carbon atoms. Also suitable are primary, secondary and tertiary amines wherein the hydrocarbyl radicals have up to about 30 carbon atoms, such as n-dodecyl amine and tri-n-hexyl amine. Also suitable are hydrocarbyl cyclo-aliphatic ethers and ketones having from 4 to 16 carbon atoms, e.g., cyclohexanone.

Other adduct-forming organic compounds useful in the present invention include nitriles, anhydrides, acid chlorides and amides having up to 30 carbon atoms. These may be represented, respectively, by the formulas $RC=N$, $(R(C:O))_2O$, $RC(:O)Cl$ and $RC(:O)NH_2$, $RC(:O)NHR$ or $RC(:O)NR_2$ where R represents a hydrocarbyl alkyl, aryl, alkaryl or an aralkyl group having up to about 30 carbon atoms. Examples are adducts of $ZrCl_4$ with n-undecane nitrile, n-decyl succinic anhydride and n-decanoyl chloride.

The second catalyst component of the present invention is an aluminum alkyl of the formulas R_2AlX , $RAlX_2$, $R_3Al_3X_3$, R_3Al or a zinc alkyl of the formula R_2Zn , where R_1 , R_2 and R_3 may be C_1 - C_{20} alkyl and X is Cl or Br . Diethylaluminum chloride, aluminum ethyl dichloride and mixtures thereof are preferred.

The process of the present invention is conducted under generally conventional oligomerization conditions of temperature and pressure, that is, about 50°C to

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250°C and about 500-5000 psig, preferably 1000 to 3500 psig for C₃ to about C₆ olefins, about 15-5000 psig for C₇ and higher olefins. Pressure is widely variable because of the differences in the olefin vapor pressures at reaction temperatures.

The process is conducted in the liquid phase. When C₃ and C₄ olefins are being oligomerized, there is employed an inert solvent which must be non-reactive with the catalyst system or in the presence of a solvent such as a liquid alpha-olefin, particularly C₆-C₁₀₀ alpha-olefins. Other suitable solvents for both olefin and catalyst include aromatic or aliphatic hydrocarbons and halogenated aromatics such as chlorobenzene, dichlorobenzene and chlorotoluene. Preferred solvents are toluene, xylenes, particularly p-xylene, and C₃-C₂₄ alkanes, especially n-heptane and n-decane. Mixtures of these solvents may also be used. Generally speaking, for C₅ and higher olefins the vapor pressure of the olefin is usually suitable so that a liquid phase reaction mixture may be maintained without the need for a solvent for the olefin reactant, but a solvent is required to act as a carrier for introduction of the catalyst into the reactor.

The amount of first catalyst component used in conducting oligomerization according to the present invention may be expressed as about 2×10^{-6} moles to about 200×10^{-6} moles of zirconium adduct catalyst component per gram of olefin being oligomerized. The second catalyst component, such as diethylaluminum chloride, is used in an amount such that the molar ratio of second component to first component is from about 15:1 to about 3:1.

The preferred temperature range to obtain oligomerization is about 120°C to 250°C. At these preferred temperatures, the pressure should be about 1000 psig in a continuous stirred tank reactor, which will produce about 10-65% conversion of olefins to dimers,

trimers and tetramers for C_3 to C_6 olefins, and about 15 to 5000 psig for C_7 or higher olefins.

In practicing the process of the present invention, the presence of water in the system should be minimized, since the catalyst of this invention is particularly sensitive to the presence of water. It has been found that only minor amounts of water will tend to produce undesirable quantities of high molecular weight polyolefins and will reduce conversions to the desired product. The amounts of water are best controlled with respect to the molar ratio of zirconium to water in the reaction mixture. The amount of water present is preferably in the range of about 20 to 1 to about 5,000 to 1 moles of zirconium per mole of water or higher. Within these desired ranges the percentage of high molecular weight (greater than 10,000) polyolefins is between 0.017 and 0.04 wt.%, based on the weight of product with conversions to product being in the range of about 55 to 70%. However, at Zr/H_2O mole ratios of 5 to 10 to 1 or less, while a conversion to desired oligomer product will occur, substantial amounts of polyolefins may be formed and reactor fouling might occur. The maximum amount of water from a practical viewpoint is considered to be a Zr/H_2O mole ratio of at least 10 to 1.

The process of the present invention will provide primarily oligomers which are dimers, trimers and tetramers of the olefin feedstock which is subjected to the process. Generally, the conversion of olefin to oligomers will be on the order of about 30 to 60% with the products comprising about 35 to 70% dimers, 10-20% trimers, 5-20% tetramers with typically 5% or less of higher molecular weight oligomers and polymeric materials. For example, hexadecene-1 may be selectively converted to oligomers comprised of about 80% dimer (C_{32} olefin) and

20% trimer (C₄₈ olefin) with only trace amounts of other products. Thus, the present invention provides an advantageous method of preparing commercially acceptable yields of olefins having specific molecular weight values.

The invention is further illustrated by the following Examples which are not to be considered as limitative of its scope.

The oligomerizations in the Examples below were conducted in a 1-liter stirred autoclave. Reactor volume was controlled at about 500 cc by a dip leg which served as the reactor exit. The autoclave was electrically heated and oil cooled. The moisture content was monitored continuously using aluminum oxide sensors. Olefin was fed continuously at a measured rate to the reactor during the test runs. Reaction solvent was dried over sieves to less than 1 ppmw and then metered continuously into the reactor. Catalyst and co-catalyst solutions were prepared in a dry box using heated and evacuated glassware to insure minimum water contamination. The zirconium catalyst was diluted in dry solvent (solvent dried to less than 1 ppmw over molecular sieves) to a concentration of about 20×10^{-6} gram moles of zirconium per gram of solution. The solutions were then transferred to the reactor feed tanks and held under a nitrogen blanket. The aluminum co-catalyst solutions were prepared from 20% by weight stock solutions obtained from a supplier. Again, dilution solvent was dried to less than 1 ppm water content before using. Co-catalyst was generally diluted to about 200×10^{-6} gram moles of aluminum per gram of solution.

EXAMPLE 1

Zirconium tetrachloride powder 80.0g, 0.343 mole, was placed in a dry glass vessel under a dry argon atmosphere. Next 125.0g of dry n-heptane solvent was

added. The resulting slurry was stirred while dry isodecyl acetate (mixed isomers sold as Exxate® 1000 by Exxon Chemical Company), 70.0g, 0.318 mole, was added dropwise over 10 minutes. There was an exotherm to about 45°C while the $ZrCl_4$ dissolved producing a hazy, pale yellow solution. The haze was due to a very small amount of inorganic impurities and unreacted $ZrCl_4$. This was filtered through a dry medium porosity glass frit under argon and the frit rinsed with 7.2g dry heptane. The combined rinse and filtrate weighed 282.2g and consisted of a clear, pale yellow solution that contained 28.3 wt.% $ZrCl_4$, in the form of a soluble complex with the isodecyl acetate.

EXAMPLE 2

Using the $ZrCl_4$ adduct prepared above in Example 1 and diethylaluminum chloride (DEAC) co-catalyst, a series of oligomerizations of propylene were carried out using the conditions set forth in Table 1 below; the results are set forth in Table 2.

EXAMPLE 3

Similar oligomerizations were carried out using 1-decene as the feedstock. The conditions are shown in Table 3 and the results in Table 4.

EXAMPLE 4

Similar oligomerization was carried out using 1-tetradecene as the olefin. Conditions are shown in Table 5 and results in Table 6.

EXAMPLES 5

The process was repeated using 1-hexadecene as the olefin. Conditions are shown in Table 7 and results in Table 8.

TABLE 1

REACTION CONDITIONS

Variable	Run 1	Run 2	Run 3	Run 4
Temperature	150 deg.C	150 deg.C	150 deg.C	150 deg.C
Pressure (a)	1000 psig	1000 psig	1000 psig	1000 psig
Propylene Feed	315 g/hr	315 g/hr	310 g/hr	410 g/hr
Solvent p-Xylene Feed	620 g/hr	620 g/hr	515 g/hr	275 g/hr
DEAC Conc. x 10 ⁻⁶ moles/g	269.1	269.1	269.1	269.1
DEAC Flow Rate	53.3 cc/hr	53.3 cc/hr	79.0 cc/hr	36.4 cc/hr
Zr Adduct Conc. x 10 ⁻⁶ moles/g	25.3	25.3	25.3	25.3
Zr Adduct Flow Rate	41.9 cc/hr	41.9 cc/hr	62.4 cc/hr	65.5 cc/hr
Al/Zr Molar Ratio	13.5	13.5	13.5	5.9
Residence Time	17 min	4 hr	1 hr	1 hr

(a) The pressure was adjusted to the indicated value by the addition of dry nitrogen gas.

TABLE 2**RESULTS**

<u>Item</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>
Productivity, g Product/g Zr	1450	2450	260	1720
Conversion	38.8%	65.5%	10.5%	52.6%
Product Distribution:				
C6	67.3%	71.0%	66.5%	38.5%
C9 estimates	21.9%	20.0%	25.4%	28.2%
C12	8.5%	6.2%	6.6%	18.9%
C15	2.2%	1.4%	1.2%	5.8%
C18	n.a.	trace	0.2%	6.4%
C21	n.a.	trace	trace	1.0%
Isomer Distribution For The Most Abundant Hexenes:				
1. 2-methyl-1-pentene	75.5%	78.6%	71.0%	54.6%
2. unidentified	9.8%	7.8%	6.6%	14.8%
3. unidentified	6.8%	5.5%	5.1%	12.3%
4. unidentified	2.3%	3.8%	5.1%	11.5%
5. unidentified	1.8%	1.3%	3.9%	1.2%
6. unidentified	1.3%	1.2%	1.7%	1.2%

TABLE 3REACTION CONDITIONS

<u>Variable</u>	<u>Run 1</u>	<u>Run 2</u>
Temperature	150 deg.C	130 deg.C
Pressure (a)	1000 psig	1000 psig
1-Decene Feed	400 g/hr	400 g/hr
DEAC Conc. x 10 ⁻⁶ moles/g	211.3	211.3
DEAC Flow Rate	41.1 cc/hr	41.1 cc/hr
Zr Adduct Conc. x 10 ⁻⁶ moles/g	38.3	38.3
Zr Adduct Flow Rate	37.6 cc/hr	37.6 cc/hr
Al/Zr Molar Ratio	5.5	5.5
Residence Time	45 min	45 min

(a) The pressure was adjusted to the indicated value by addition of dry nitrogen gas.

TABLE 4RESULTS

<u>Item</u>	<u>Run 1</u>	<u>Run 2</u>
Productivity, g Product/g Zr	2014	1766
Conversion	58.4%	51.2%
Product Distribution		
C20	73.3%	69.8%
C30	20.5%	23.2%
C40	6.1%	7.0%
Isomer Distribution For The Most Abundant C20 Olefins		
1. unidentified	63.9%	65.3%
2. unidentified	17.9%	17.2%
3. unidentified	8.7%	8.6%
4. unidentified	6.8%	5.2%
5. unidentified	0.8%	1.0%

TABLE 5REACTION CONDITIONS

<u>Variable</u>	<u>Run 1</u>
Temperature	150 deg.C
Pressure (a)	1000 psig
1-Tetradecene Feed	470 g/hr
DEAC Conc. x 10 ⁻⁶ moles/g	289.4
DEAC Flow Rate	30.1 cc/hr
Zr Adduct Conc. x 10 ⁻⁶ moles/g	40.9
Zr Adduct Flow Rate	34.2 cc/hr
Al/Zr Molar Ratio	6.2
Residence Time	45 min

(a) The pressure was adjusted to the indicated value by the addition of dry nitrogen gas.

TABLE 6RESULTS

<u>Item</u>	<u>Run 1</u>
Productivity, g Product/g Zr	2372
Conversion	56.7%
Product Distribution	
C28	83.5%
C42	16.5%
Isomer Distribution For The Most Abundant C28 Olefins	
1. unidentified	65.7%
2. unidentified	15.1%
3. unidentified	7.9%
4. unidentified	4.7%
5. unidentified	1.2%

TABLE 7REACTION CONDITIONS

<u>Variable</u>	<u>Run 1</u>
Temperature	150 deg.C
Pressure (a)	1000 psig
1-Hexadecene Feed	535 g/hr
DEAC Conc. $\times 10^{-6}$ moles/g	287.0
DEAC Flow Rate	30.6 cc/hr
Zr Adduct Conc. $\times 10^{-6}$ moles/g	42.2
Zr Adduct Flow Rate	33.5 cc/hr
Al/Zr Molar Ratio	6.2
Residence Time	1 hr

(a) The pressure was adjusted to the indicated value by the addition of dry nitrogen gas.

TABLE 8RESULTS

<u>Item</u>	<u>Run 1</u>
Productivity, g Product/g Zr	2803
Conversion	58.7%
Product Distribution	
C32	80.0%
C48	20.0%
Isomer Distribution For The Most Abundant C ₃₂ Olefins	
1. unidentified	64.2%
2. unidentified	15.7%
3. unidentified	7.7%
4. unidentified	5.1%
5. unidentified	1.7%

CLAIMS:

1. A process for conducting the oligomerization of C_3 and higher olefins which comprises oligomerizing said olefins in the presence of a homogeneous two component catalyst, the first component being an adduct of $ZrCl_aBr_b$, where $a+b=4$ and a or b may be 0, 1, 2, 3 or 4, with an organic compound selected from the group consisting of esters, ketones, ethers, amines, nitriles, anhydrides, acid chlorides, amides or aldehydes, said organic compound having up to 30 carbon atoms and the second component being an alkyl metal catalyst selected from the group consisting of R_2AlX , RA_2X_2 , $R_3Al_2X_3$, R_3Al and R_2Zn wherein R is C_1 - C_{20} alkyl and X is Cl or Br , the oligomerization being conducted in a reactor vessel at $50^\circ C$ to $300^\circ C$ at a pressure of about 15 to 5000 psig in the liquid phase, with the presence of water in the reactor vessel being minimized such that the ratio of moles of zirconium to moles of water is at least 10 to 1.

2. The process of claim 1 wherein the amount of said zirconium adduct is about 1×10^{-6} to 200×10^{-6} moles per gram of olefin being oligomerized.

3. The process of claim 2 wherein the molar ratio of said alkyl metal catalyst to said zirconium adduct is about 15:1 to 3:1.

4. The process of claim 1 wherein the olefin is a C_3 - C_{20} linear aliphatic hydrocarbyl monounsaturated olefin.

5. The process of claims 1, 2, 3 or 4 wherein said organic compound is an ester of the formula R_1COOR_2 wherein R_1 and R_2 represent alkyl, aryl, alkaryl or aralkyl groups having a total of 1 to 30 carbon atoms and R_1 may be also H.

6. The process of claim 5 wherein said organic compound is an acetate ester of the formula CH_3COOR_1 where R_1 has about 6 to 16 carbon atoms and the adduct is of the formula $(ZrCl_4 \cdot CH_3COOR_1)_2$.

7. The process of claims 1, 2, 3 or 4 wherein said adduct is an adduct of $ZrCl_4$.

8. The process of claim 6 wherein the acetate ester is a mixture of isomers of isodecyl acetate.

9. The process of claim 1 wherein said ketones have the formula $R_1C(:O)R_2$ where R_1 and R_2 represent alkyl, aryl, alkaryl or aralkyl groups having a total of 1 to 30 carbon atoms or a cyclo aliphatic hydrocarbyl group having 4 to 16 carbon atoms.

10. The process of claim 1 wherein said ethers have the formula R_1OR_2 where R_1 and R_2 represent alkyl, aryl, alkaryl and aralkyl groups having a total of 1 to 30 carbon atoms or a cyclo aliphatic hydrocarbyl group having 4 to 16 carbon atoms.

11. The process of claim 1 wherein said aldehydes have the formula $R_1C(:O)H$ where R_1 represents alkyl, aryl, alkaryl and aralkyl groups having 1 to 30 carbon atoms.

12. The process of claim 1 wherein said nitriles have the formula $RC=N$ wherein R represents alkyl, aryl, alkaryl and aralkyl groups having a total of 1 to 30 carbon atoms.

13. The process of claim 1 wherein said anhydrides have the formula $(R-C(:O))_2O$ wherein R represents alkyl, aryl, alkaryl and aralkyl groups having a total of 1 to 30 carbon atoms.

14. The process of claim 1 wherein said acid chlorides have the formula $RC(:O)Cl$ where R represents alkyl, aryl, alkaryl and aralkyl groups having a total of 1 to 30 carbon atoms.

15. The process of claim 1 wherein said amides have the formulas $RC(:O)NH_2$, $RC(:O)NHR$ and $RC(:O)NR_2$ where R represents alkyl, aryl, alkaryl and aralkyl groups having a total of 1 to 30 atoms.

16. The process of claims 1, 2, 3 or 4 wherein the olefin is propylene.

17. The process of claims 1, 2, 3 or 4 wherein there is present a solvent which comprises p-xylene, mixed xylenes, or n-decane.

18. The process of claims 1, 2, 3 or 4 wherein the alkyl metal catalyst is diethylaluminum chloride, aluminum ethyl dichloride or mixtures thereof.

19. The process of claims 1, 2, 3 or 4 wherein the olefin is 1-decene.

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C07C2/30; B01J31/38		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C07C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 295 960 (EXXON CHEMICAL PATENTS) 21 December 1988 see claims; examples	1-19
A	GB,A,2 152 403 (CHEVRON RESEARCH) 7 August 1985 see claims; examples	1-19
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold;">22 JULY 1992</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold;">19 0. 88</div>	
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">ZERVAS B. <i>Brigitte Zervas</i></div>	

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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9201821
SA 58537**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 22/07/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0295960	21-12-88	US-A- 4855525	08-08-89
		AU-B- 598676	28-06-90
		AU-A- 1697888	22-12-88
		CN-A- 1052119	12-06-91
		JP-A- 1063532	09-03-89
		US-A- 4966874	30-10-90
GB-A-2152403	07-08-85	US-A- 4579991	01-04-86
		CA-A- 1237117	24-05-88
		DE-A- 3500638	18-07-85
		FR-A- 2558073	19-07-85
		JP-A- 60174731	09-09-85
		US-A- 4870041	26-09-89

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